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Novel basalt fibre reinforced glass matrix composites

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A novel hot-pressing technique for the manufacturing of basalt fibre reinforced glass matrix composites was investigated. Two-dimensional (2D) fibre mats were sandwiched between borosilicate glass powder layers, thus configuring a much simpler processing route than that commonly employed for the production of fibre-reinforced glasses. Besides economic benefits, the use of fibre mats may lead to technologic advantages due to the possibility of readily coating the fibres with a suitable material (e.g. titanium oxide) by means of the sol-gel method. The coating of basalt fibre mats with TiO_2 is proposed for preventing the fibres from an excessive adhesion to the glass matrix. The developed composites containing 15 vol% of 2D-fibre reinforcement exhibited promising bending strength (~90 MPa) and desirable "graceful" fracture behaviour without catastrophic failure. Thus the present study represents a convenient approach for production of advanced low-cost fibre reinforced glass matrix composites for structural applications.

1. Introduction

Glass matrix composites reinforced with oxide fibre have not been investigated as much as their counterparts with SiC and C fibres [1, 2]. Although oxide fibres, such as glass fibres, basalt fibres and alumina-based fibres, generally possess a remarkable tensile stress, their employment in the manufacturing of glass matrix composites is strongly limited by the development of a strong fibre-matrix interfacial bond. In the case of a strong bond, the fibres cannot undergo debonding and pull-out, with a strong absorption of fracture energy upon the cracking of the glass matrix, but they are subjected to direct fracture as cracks propagate unimpeded from the matrix [3]. As a consequence, the improvement of mechanical properties provided by the fibrous reinforcement, especially regarding fracture toughness, is severely restricted. In order to achieve a relatively weak fibre-matrix interface some "lubricating" coatings such as carbon from polymer pyrolysis or chemical vapour deposition [3], or tin dioxide and boron nitride from chemical vapour deposition [4–6] have been proposed. In practice, the interfacial bond must be tailored in order to be sufficiently high for the load transfer between the matrix and the fibres but not too strong to allow direct fracture propagation through the interface [4]. It should be noted, however, that the nature of the coating may be detrimental to other important properties of composites, like for example the oxidation resistance (if the coating is a not an oxide material), or it may cause a more complex and expensive manufacturing of the composites (for example, fibres with carbon coatings must be treated in selected non oxidising atmospheres) [2, 4].

The reinforcement of glasses with oxide fibres has recently become of topical interest for the development of a new kind of inorganic composites, named "optomechanical composites" [7–10]. In these composites the improvement of the bending strength and fracture toughness provided by the fibres should be accompanied by a transparent or translucent appearance, in order to achieve useful materials for numerous applications in optics and in the building industry,

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as both structural and light transmitting materials, in armour windows, windshields and high-impact resistance monitoring windows [7]. SiC and carbon fibres, which represent the most common fibrous reinforcements of glasses and glass-ceramics, cannot be employed as the composites become opaque. Since oxide fibres represent the chosen reinforcement for optomechanical composites, the above described coating of fibres, essential for the optimal coupling with glass matrices, should not modify the transparent or translucent appearance. Moreover, a certain attention should be paid to the economy and the complexity of composites manufacturing; economic coatings and economic processing routes are of interest for industrial applications. Concerning this aspect, a recent work [7] demonstrated the feasibility of fabricating composites by a simple "sandwiching" method based on the bonding of glass sheets embedding individually aligned basalt and alumina fibres. The method however allowed only for the fabrication of composites with relative low volume fraction of fibres (<5 vol%).

In this work we present the production and characterisation of novel glass matrix composites fabricated by hot-pressing of fine glass powders embedding basalt 2-directional (2-D) fibre mats. The use of fibre mats is advantageous as a sol-dipping process can be easily adopted to produce adequate oxide sol-gel based coatings on the individual fibres. In addition, the use of fibre mats provides a much simpler and more economic composite manufacturing approach when compared to that commonly employed for the production of unidirectional fibre-reinforced glasses, which consists of fibre impregnation through a slurry of powdered matrix glass, winding of fibres, stacking of laminae, and consolidation by hot-pressing [4, 11]. In this paper, the details of the composite manufacturing and preliminary investigations of their mechanical properties are presented and discussed.

2. Experimental

2.1. Materials

Borosilicate recycled glass cullet (Kimble/Kontes, Vineland, NJ, USA) was employed as the matrix. This type of glass is currently intended for pharmaceutical applications. The relatively high alumina content is useful for preventing the glass from devitrification; it is well throw that alumina and zirconia may act as crystallization inhibitors in borosilicate glass [12]. The chemical composition and the physical properties of the investigated glass are shown in Table I [13, 14].

The glass cullet was first dry milled and sized in order to obtain particles of size <37 μm, then the powder was ground in a tungsten carbide vibratory mill for 15 min, producing fine glass particles with a diameter <20 μm.

Commercially available 2-dimensional basalt fibre mats (NIIgrafit, Moscow, Russia) were employed as the reinforcement. The areal weight of the mats was about 220 g/m^2. A typical chemical composition of basalt rock employed for the manufacturing of fibres is reported in Table I [15]. The basalt fibres had a diameter of about 10 μm. The maximum working temperature of the fibres is 700°C, and the tensile strength is estimated to be about 1.5 GPa [16].

TABLE I Chemical composition and physical properties of the glass matrix and the fibre reinforcement used

	Borosilicate glass	Basalt fibre
Chemical composition (wt. %)		
SiO_2	72	51.6–57.5
B_2O_3	12	
Al_2O_3	7	8.2–16.9
CaO	1	5.2–7.8
MgO		1.3–3.7
Na_2O	6	2.5–6.4
K_2O	2	0.8–4.5
BaO	<0.1	
Fe_2O_3		4.0–9.5
Physical properties		
Dilatometric softening point	650°C	
Thermal expansion coefficient	5.5×10^{-6}°C^{-1}	8.01×10^{-6}°C^{-1}
Young's modulus	72 GPa	82–110 GPa
Density	2.33 g/cm^3	2.65 g/cm^3

In order to limit the adhesion between the glass matrix and the reinforcement, the fibre mats were coated with a ceramic layer of TiO_2 using a sol-gel method (see below). As previously reported in the literature [7], titanium oxide is an effective interfacial agent between borosilicate glass and ceramic fibres. Although a certain load transfer between the matrix and the reinforcement is allowed, the coating is intended to cause the debonding and pull-out of the fibres as the microcracking of the matrix proceeds, thus contributing to a remarkable dissipation of fracture energy within the composite material.

2.2. Fibre coating

The TiO_2 coating was prepared from a solution of titanium (IV) tetra-butoxide (Aldrich chemicals) in ethyl alcohol [17]. Acetyl-acetone was employed as a chelating agent, while distilled water was used for hydrolysation. The preparation of the coating solution, which led to a TiO_2 final concentration of 40 g/l, is shown in Fig. 1.

The basalt fibre mats were cut in square pieces (50 mm×50 mm), fixed on paper frames and dipped into the coating solution. The coating speed was 10 mm/min. The fibres were dried for 0.5 h in air at room temperature and 24 h at 60°C, in order to remove most of the solvent. Finally, the fibres were heat-treated at 500°C for 1 h, in order to remove completely the solvent and to partially densify the titanium oxide layer. Scanning electron microscopy (SEM) (Philips XL 30 ESEM) was used to investigate the quality of the coatings.

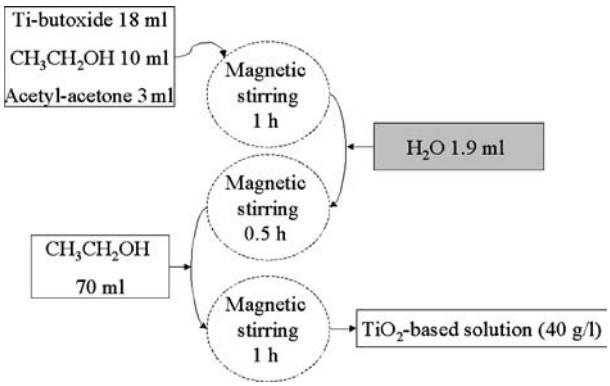

Figure 1 Sol-gel procedure for the preparation of a TiO_2-based solution for the coating of basalt fibre mats.

2.3. Composite fabrication

A novel method of composite fabrication was adopted by sandwiching the TiO_2 coated mats between layers of fine glass powder and subsequently hot-pressing in vacuum. Five layers of TiO_2 coated basalt fibre mats were sandwiched between 6 layers of glass powder inside a graphite die with a diameter of 38 mm. The weight of the layers was calculated in order to fix the volume fraction of fibres at 15 vol%. The basalts fibre mats were carefully orientated in order to maintain the fibres parallel in all layers, as shown in Fig. 2.

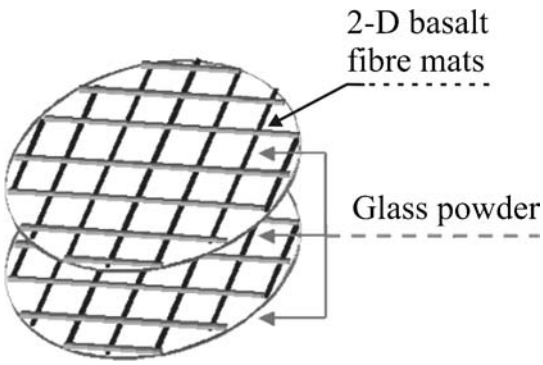

Figure 2 Orientation of the fibre mats inside the graphite die for hot-pressing.

The composites were subjected to a slow heating (2°C/min) up to 670°C, held at this temperature for 2 or 4 h and cooled down to room temperature with a rate of about 4°C/min. A pressure of 10 MPa was applied when the temperature reached the maximum level and removed at the end of the holding time. In order to facilitate removal of the composite samples after the hot-pressing treatment, the graphite die was coated with boron nitride. For comparison, also glass powder without any reinforcement was subjected to the same treatment.

The density of the hot-pressed glass matrix composites was measured by the Archimedes' principle. At least ten fragments were analysed for each sample. The theoretical densities of composite materials were calculated from the density of the constituents by applying the rule of mixtures.

Beam samples of about 3 mm×2.5 mm×30 mm for bending strength determination were cut from hot-pressed discs. It should be noted that the composite materials were cut along one of the fibre directions in the basalt fibre mats. All samples were carefully polished to a 6 μm finish by using abrasive papers and diamond paste. The edges of the bars were bevelled by using diamond paste. Four point bending tests (28 mm outer span, 8 mm inner span) were performed using an Instron 1121 UTS rig (Instron Danvers, MA), with a crosshead speed of 0.2 mm/min. At least 5 individual tests were carried out and the results averaged.

The fracture surfaces of tested samples were observed by scanning electron microscopy (SEM) (Philips XL 30 ESEM).

3. Results and discussion

Typical sol-gel TiO_2 coating on basalt fibres are shown in Fig. 3; the relative fluorescence spectrum demonstrates the presence of Ti, qualitatively indicating the effectiveness of

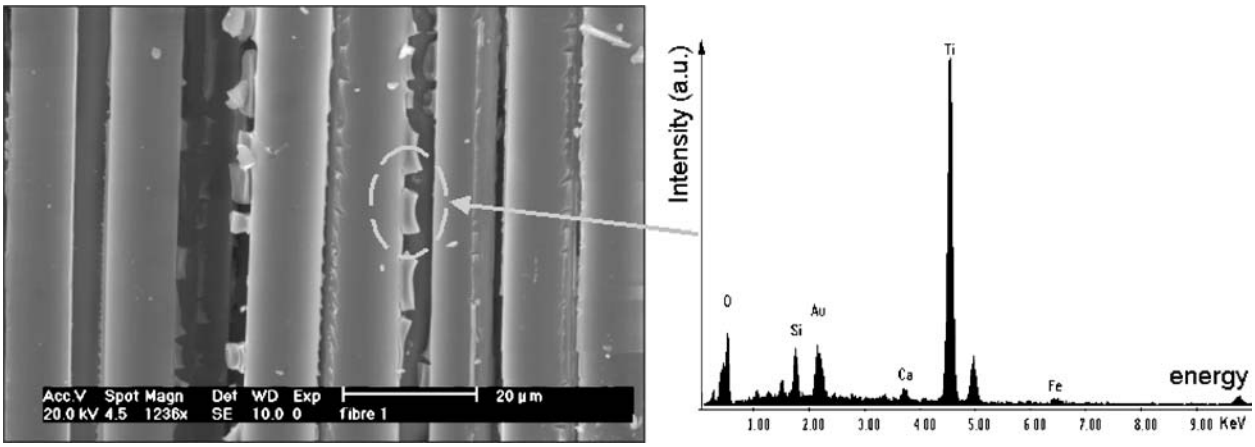

Figure 3 SEM micrograph of the TiO_2 coated basalt fibres with the fluorescence (energy dispersive x-ray analysis) spectrum of the selected area. Microcracking of the inorganic coating between the fibres is observed (marked by the arrow).

TABLE II Summary of measured data on hot-pressed materials: bending strength, density and porosity

	Processing Parameters	Bending strength (MPa)	Density (g/cm^3)	Porosity %
Un-reinforced glass	2 h @ 670°C	80±10	2.34±0.02	0.00
Basalt fibre reinforced composite	2 h @ 670°C	71±11	2.38±0.02	0.18
Basalt fibre reinforced composite	4 h @ 670°C	90±6	2.37±0.02	0.65

Figure 4 Flexural specimen of basalt fibre reinforced glass matrix composite after rupture; the glass matrix fragments are "bridged" by the reinforcing fibres, without catastrophic failure.

the coating procedure. It should be noted however that the coating was not uniform, probably due to a not adequate viscosity of the coating solution during the dipping phase. Moreover some cracking of the coating between the fibres and at the points of thicker deposition was observed, as seen in Fig. 3.

The working temperature for composite manufacturing was chosen to be 670°C as a compromise between the dilatometric softening temperature of the glass matrix (650°C) and the declared maximum working temperature for basalt fibres (700°C). It is well known that the lower limit for the densification of glass powders is the dilatometric softening point of the glass, at which the contraction of a sample due to viscous flow is exactly counterbalanced by the thermal expansion. The enhanced compaction provided by the hot-pressing procedure was thought to enable a high densification degree of the samples at the chosen temperature. Indeed the hot-pressed materials exhibited optimum densification, as they practically reached theoretical density, thus confirming the preliminary hypothesis on the suitable processing temperature chosen for composite manufacturing.

The bending strength data of the hot-pressed materials are summarized in Table II. It is seen that the bending strength of the composites exceeded that of un-reinforced glass only in the case of a hot-pressing treatment of 4 h at 670°C. One possible reason for this result is that the glass infiltration in the inter-fibre spaces might be more effective in the composite prepared using a longer hot-pressing treatment. The achieved bending strength is promising, since the samples had a certain fraction of fibres in the transverse direction, which do not contribute to strengthening and might act as a discontinuity. In addition, the tensile strength of basalt fibres is much lower than that of other ceramic fibres (for example alumina-based fibres).

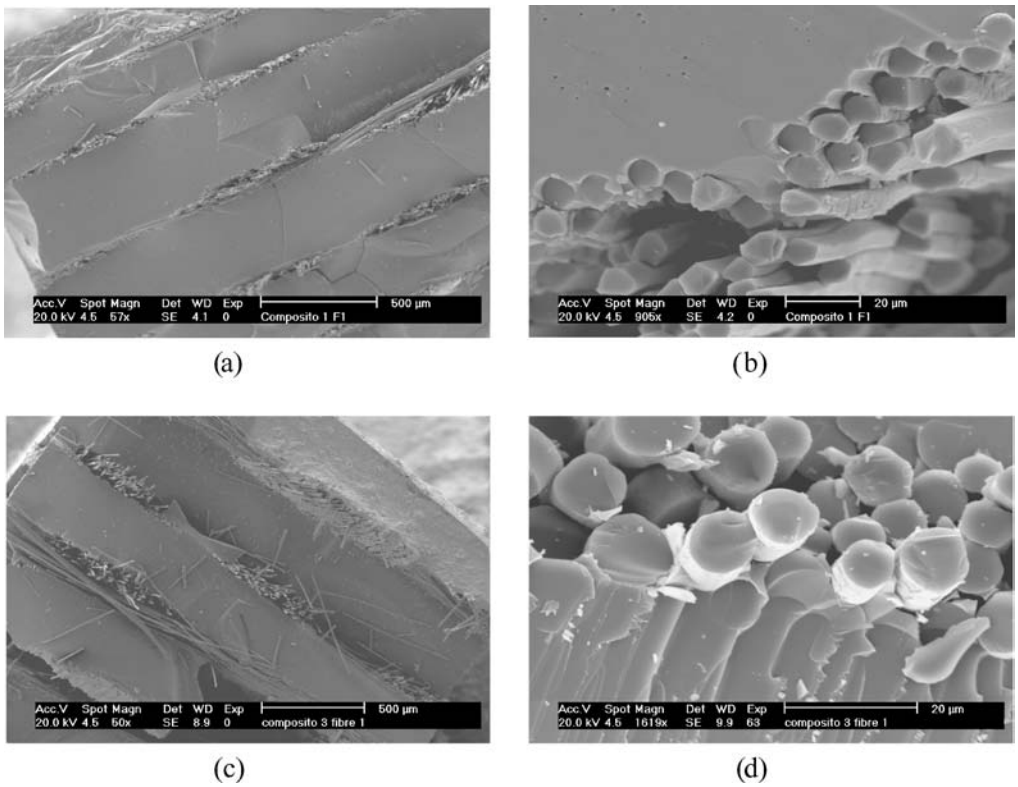

Figure 5 Fracture surfaces of (a, b) composite material manufactured by hot-pressing at 670°C for 2 h; (c, d) composite material manufactured by hot-pressing at 670°C for 4 h.

The evaluation of mats with a preferential fibre orientation or non-woven mats could be advantageous and it will be the focus of further developments.

It must be emphasized that the composites underwent rupture without catastrophic failure of the flexural samples. The fibre mats, as illustrated in Fig. 4, had a bridging effect holding the cracked glass matrix fragments. This is a typical behaviour of wired glass, i.e. glasses with an embedding metallic mesh, which are generally employed in the building industry as safety glass [18]. It is known, however, that wired glass possess poor mechanical properties in tension when compared to un-reinforced glass due to imperfections at the glass/metal interface [19]. The bending strength and fracture behaviour of the composites fabricated here indicate that the reinforcement of glass with ceramic mats might represent a valid alternative to standard wired glass. Moreover, the proposed fabrication approach could be useful for the production of translucent "optomechanical" glass matrix composites with 2-D reinforcement with higher fibre volume fraction than that achieved by other methods [7].

The fracture surfaces of the composites are shown in Fig. 5.

The low magnification images (Fig. 5a and c) show the previously mentioned 2-D distribution of the fibres. The high magnification images (Fig. 5b and d) demonstrate limited debonding and pull-out of the fibres, even if an effective glass infiltration of the fibre mats was achieved. One likely reason for the limited sliding of the fibres is the observed microcracking of the TiO_2 coating (Fig. 3), which causes un-coated fragments of fibres to be strongly anchored to the matrix thus making more difficult the fibre pull-out mechanism. As previously mentioned, a new chemical formulation of the sol-gel precursor solution for coating of fibres may be required to achieve a solution with a more adequate viscosity, leading to more homogeneous and continuous TiO_2 coating: solutions with a lower viscosity could infiltrate the spaces between the fibres in the mats in a more effective way.

4. Conclusions

The reported research was a preliminary study on the manufacturing of a new generation of 2-D ceramic fibre reinforced glass matrix composites, obtained by a much simpler fabrication route than the currently employed. The key feature of the study was the use of cost effective 2-D basalt fibre mats, which enabled the readily coating of individual fibres with a TiO_2 layer using a sol-gel dipping method. The mechanical properties and the fracture behaviour of the obtained composites are promising, especially when related to the relatively poor homogeneity of the TiO_2 coating achieved. The use of more temperature resistant ceramic fibre mats, with different fibre architectures, and the development of more adequate coating solutions will be the object of future experiences.

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